Depth, radiocarbon, and the effectiveness of direct CO_2 injection as an ocean carbon sequestration strategy

Ken Caldeira,[1] Michael E. Wickett,[2] and Philip B. Duffy[1]

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[1] If radiocarbon were a good predictor of the amount of time until a water parcel returns to the surface, it could be used to estimate the effectiveness of carbon sequestration by direct injection. We performed direct CO_2 injection simulations in both one-dimensional box-diffusion and three-dimensional ocean general circulation models. The 1-D model results for ocean carbon retention accord with the 3-D model results, especially in the Pacific basin and at shallower depths. In the 1-D model, carbon retention in the ocean is directly related to both the injection depth and the $\Delta^{14}C$ of carbon at the injection location. However, in the 3-D model, depth, but not radiocarbon, provides a relatively good prediction of carbon retention. This suggests that the expected time for a water parcel to return to the surface is closely related to its depth and not in general to the time since last at the surface. *INDEX TERMS:* 4255 Oceanography: General: Numerical modeling; 4263 Oceanography: General: Ocean prediction; 4806 Oceanography: Biological and Chemical: Carbon cycling; 1635 Global Change: Oceans (4203)

1. Introduction

[2] Direct injection of CO_2 into the ocean interior has been proposed as an approach to slow the accumulation of carbon dioxide in the atmosphere and thus global warming. The idea of this approach is to inject fossil-fuel carbon dioxide into the ocean interior, thereby bypassing the mixing processes that would otherwise cause a relatively slow transfer of excess atmospheric CO_2 to the deep ocean [e.g., *Caldeira and Duffy*, 2000; *Herzog et al.*, 2001]. This approach was first proposed by *Marchetti* [1977] and was first modeled by *Hoffert et al.* [1981] using a one-dimensional upwelling-diffusion ocean model. One area of ongoing research is to predict how long carbon will be retained in the ocean as a function of the location and depth of CO_2 injection [e.g., *Orr et al.*, 2001b].

[3] Radiocarbon, or ^{14}C, is created in the stratosphere as cosmic rays collide with atmospheric nitrogen. Some of this ^{14}C passes through the ocean surface, decaying as it ages in the deep ocean. The ratio of ^{14}C to ^{12}C, corrected for mass-dependent fractionation processes and normalized to a reference standard, is denoted $\Delta^{14}C$, and can be divided into natural, bomb, and Suess components [*Broecker and Peng*, 1982]. In this paper, we refer only to the natural component of $\Delta^{14}C$ for simplicity. Typically, the radiocarbon content of dissolved inorganic carbon in the ocean is related to the amount of time that has passed since that parcel of water was last in contact with the atmosphere. At the ocean surface, $\Delta^{14}C$ values are typically -50 per mil, and in the old deep interior waters of the North Pacific ocean these values reach a minimum of less than -240 per mil, suggesting an aging of $\sim$1845 years. However, interpretation of age is complicated by incomplete equilibration of surface waters with the atmosphere and by mixing of water masses in the ocean interior.

[4] This paper addresses three related questions: (1) How well can the effectiveness of direct CO_2 injection as a carbon sequestration strategy be predicted from radiocarbon content alone? (2) How well can the effectiveness of direct CO_2 injection be predicted from the injection depth alone? (3) How well can a one-dimensional box-diffusion model simulate retention of injected carbon in the ocean? We address these questions by comparing results from direct CO_2 injection simulations using one- and three-dimensional ocean models.

2. Ocean Circulation and Radiocarbon

[5] *Oeschger et al.* [1975] proposed that ocean carbon uptake could be simulated using a discretized form of a single one-dimensional diffusive column—a one-dimensional box-diffusion model of the global ocean carbon cycle. In such a model, all transport is diffusive; there is no advective or convective transport. Variants of this original model have proven quite useful in simulating various properties of the ocean carbon cycle [e.g., *Hoffert et al.*, 1981; *Siegenthaler*, 1983; *Caldeira et al.*, 1998; *Caldeira and Duffy*, 2000].

[6] In contrast, *Broecker and Peng* [1982] proposed that the circulation of the ocean can be conceptualized as a conveyer belt, in which water sinks in the North Atlantic and is advected through the deep ocean to upwell at lower latitudes. The concept of the conveyer belt circulation has been developed and modified [e.g., *Schmitz*, 1995] and has proven quite influential in shaping our thinking about the response of the global ocean to increasing atmospheric CO_2 content [e.g., *Manabe and Stouffer*, 1995] and its response to changes in ocean circulation [e.g., *Sarmiento et al.*, 1998].

[7] These two end-member conceptualizations of ocean circulation (i.e., diffusive versus conveyer belt) have very different implications for the relationship between radiocarbon content and the effectiveness of a site for carbon sequestration via direct CO_2 injection. In a purely diffusive ocean, the most effective place to inject carbon would be the location with the "oldest" radiocarbon. In this case, the

[1]Climate and Carbon Cycle Modeling Group, Lawrence Livermore National Laboratory, Livermore, California, USA.
[2]Center for Applied Scientific Computing, Lawrence Livermore National Laboratory, Livermore, California, USA.

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time to diffuse down from the surface would be equal to the time to diffuse back up to the surface, $\Delta^{14}C$ values decrease monotonically with depth [*Caldeira et al.*, 1998], and sequestration effectiveness increases monotonically with depth [*Herzog et al.*, 2001]. In contrast, if ocean circulation behaved as a single advective conveyer belt, the "oldest" radiocarbon would be the radiocarbon that is soon to be exposed to the atmosphere. In this case, waters would be oldest just prior to resurfacing, and the most effective sequestration location would be relatively young waters (i.e., with relative high $\Delta^{14}C$ values) that had just recently been isolated from the atmosphere.

[8] Of course, the ocean has many pathways by which water parcels are transported from the surface to the interior, mixed with other parcels, and returned to the surface. Therefore, the ocean behaves neither as a purely diffusive medium nor as a simple conveyor belt.

3. Model Description and Simulations

[9] We performed a set of natural radiocarbon and direct CO_2 injection simulations in both a one-dimensional box-diffusion model and a three dimensional global general circulation model.

[10] We used the one-dimensional box-diffusion model [*Oeschger et al.*, 1975; *Siegenthaler*, 1983] described in more detail in *Caldeira et al.* [1998]. It has a 75 m thick mixed-layer and a total depth of 3800 m. The state variables are ^{12}C, ^{13}C and ^{14}C masses or concentrations. The eddy diffusion and gas-transfer velocity coefficients were chosen such that the change in ocean $\Delta^{14}C$ inventory between 1945 and 1975 matches the estimated 1975 bomb radiocarbon inventory [*Broecker et al.*, 1995] of 305×10^{26} atoms, and the modeled 1975 ocean mean and surface ocean $\Delta^{14}C$ matches the basin-volume-weighted mean of the natural plus bomb $\Delta^{14}C$ values measured in the GEOSECS program [*Broecker et al.*, 1985]. This tuning yielded a vertical eddy diffusion coefficient of 8,820 $m^2\ yr^{-1}$ at the base of the mixed-layer, diminishing with an *e*-folding length scale of 500 m to a minimum of 2,910 $m^2\ yr^{-1}$ at the ocean bottom. The tuned gas transfer velocity is equivalent to 0.0543 mol $m^{-2}\ \mu atm^{-1}\ yr^{-1}$ at 18°C.

[11] The three-dimensional simulations were performed using the LLNL ocean general circulation model, which is based on the GFDL Modular Ocean Model (MOM) [*Pacanowski et al.*, 1991] and is coupled to the sea ice model of *Oberhuber* [1993]. The model configuration and steady-state results are the same as those described in more detail in *Caldeira and Duffy* [2000] and *Duffy et al.* [1997]. These simulations use a mesh of 2° (latitude) by 4° (longitude) with 23 vertical levels, and the model was tuned to approximately simulate the $\Delta^{14}C$ values observed in the deep central North Pacific ocean. Broad spatial patterns in $\Delta^{14}C$ are well represented by this model; however, $\Delta^{14}C$ is affected by relatively weak and shallow North Atlantic deep water production. The configuration shown here is LLNL's entry in the Ocean Carbon-cycle Model Intercomparison Project (OCMIP).

[12] Both of these models were run under the radiocarbon and sequestration scenarios described in the OCMIP protocols. In the sequestration scenario, the atmospheric CO_2 concentration was specified to be the IPCC S650 scenario, and the injected CO_2 that leaks out to the atmosphere is not permitted to re-enter the ocean as it would in the real world. 21 injection cases were simulated—7 injections at 3 different depths—each at a rate of 0.1 PgC yr^{-1} for 100 years starting in year 2000 and continuing another 400 years with no injection. Injection locations are near the Bay of Biscay, New York City, Rio de Janeiro, San Francisco, Tokyo, Jakarta, and Bombay. Injection depths are approximately 800 m, 1500 m, and 3000 m.

4. Results and Discussion

[13] The basic results for the model simulations are presented in Figure 1. The figure represents the amount of injected carbon remaining in the ocean as a function of time. With perfect retention the lines would slope up at 0.1 PgC yr^{-1} until year 100 and then remain at 10 PgC thereafter. The top, middle, and bottom panels show results for injections at 800 m, 1500 m, and 3000 m depth, respectively. Injection at 3000 m is quite effective at sequestering carbon from the atmosphere for several centuries, whereas injection at shallower depths is less effective. In general, injections into the Pacific Ocean (i.e., San Francisco and Tokyo) are more effective than injection at the same depth in the Atlantic Ocean (i.e., New York City, Rio de Janeiro, and the Bay of Biscay). As can be seen from the results at 100 years, sequestration effectiveness is more dependent on injection location for shallower injections.

[14] The one-dimensional box-diffusion model well represents the average behavior of the three-dimensional model at 800 m and 1500 m, but somewhat overpredicts retention at 3000 m (Table 1). This difference at depth is due to the lack of advection in the box-diffusion model to more rapidly bring carbon from the deep ocean to the ocean surface. The results of the 1-D model for the 3000 m injection agree best with the 3-D model results for the Pacific Ocean injections. This suggests that large-scale advective processes may be more important in bringing deep water to the surface in the Atlantic basin than the Pacific basin.

[15] In Figure 2 and Table 1, we show the depth, $\Delta^{14}C$, and the amount of injected carbon remaining in the ocean after 500 years of simulation. This amount is closely related to injection depth in both models. As a result of the calibrated covariation of depth and $\Delta^{14}C$, the 1-D model displays a very direct relationship between the $\Delta^{14}C$ of dissolved inorganic carbon and the amount of carbon remaining after 500 years.

[16] A regression of 500 year retention with injection depth from the 3-D model (Figure 2a) yields a strong correlation ($R^2 = 0.909$). A regression of 500 year retention with $\Delta^{14}C$ at the injection location from the 3-D model (Figure 2b) yields a much weaker correlation ($R^2 = 0.30$). Given either a depth or $\Delta^{14}C$ value at another injection location, the shaded gray areas in the figure represent the range of injected carbon remaining that can be predicted with 95% confidence based on the 21 injection simulations performed in the 3-D model.

[17] Further, a regression of 500 year retention with both injection depth and $\Delta^{14}C$ at the injection location from the 3-D model (not shown) yields only a slightly stronger correlation than depth alone ($R^2 = 0.913$). This result

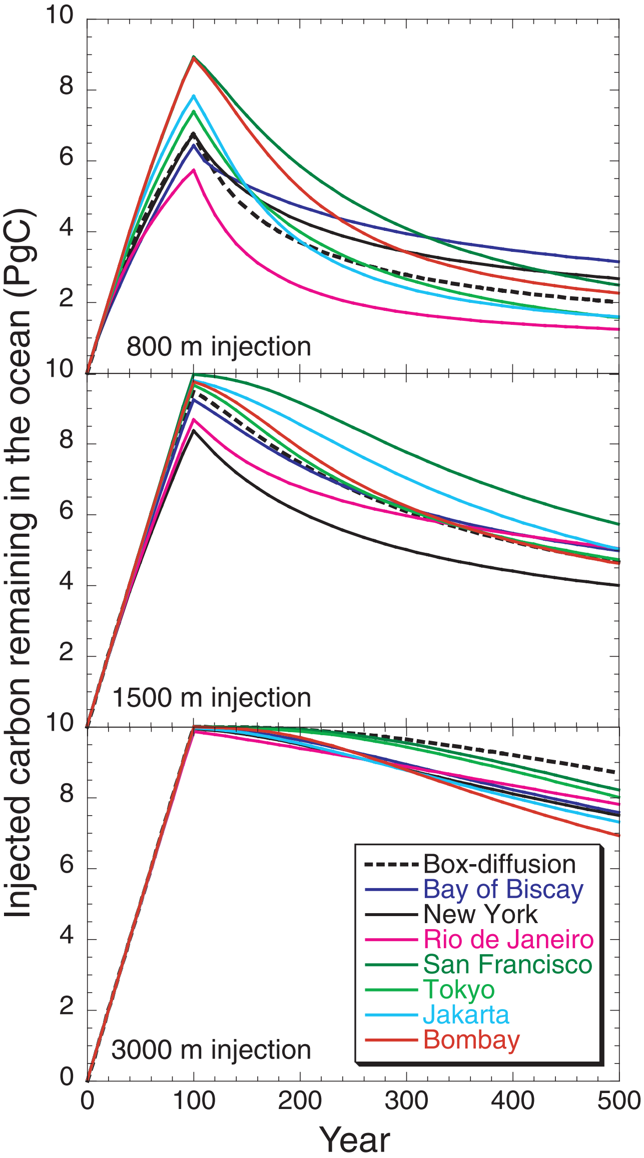

Figure 1. Results of direct CO_2 injection simulations performed using a one-dimensional box-diffusion model and a three-dimensional ocean GCM. Injections were made at three different depths and, in the case of the GCM, at seven different locations. 10 PgC was released uniformly in each case over 100 years. Sequestration effectiveness increases with depth of injection. The 1-D model results are broadly consistent with the 3-D model results.

Table 1. Comparison of 1-D and 3-D Model Results

	Box-diffusion		Ocean GCM	
Depth (m)	$\Delta^{14}C$ (per mil)	Percent retained	$\Delta^{14}C$ (per mill)	Percent retained
800	−94	20	−114 ± 46	21 ± 7
1500	−144	46	−156 ± 73	49 ± 7
3000	−216	87	−193 ± 42	76 ± 7

Results from the 1-D box-diffusion model and the 3-D ocean general circulation model for radiocarbon and percentage of injected carbon retained after 500 years of simulation. Ocean GCM results represent the mean and standard deviation of seven injections at each depth.

suggests that depth of injection is a good predictor of oceanic retention of injected carbon, but that knowing the $\Delta^{14}C$ of the dissolved inorganic carbon at that location does not contribute significantly to improving the accuracy of predicted carbon retention. Nevertheless, radiocarbon could contribute to determining the effectiveness of direct CO_2

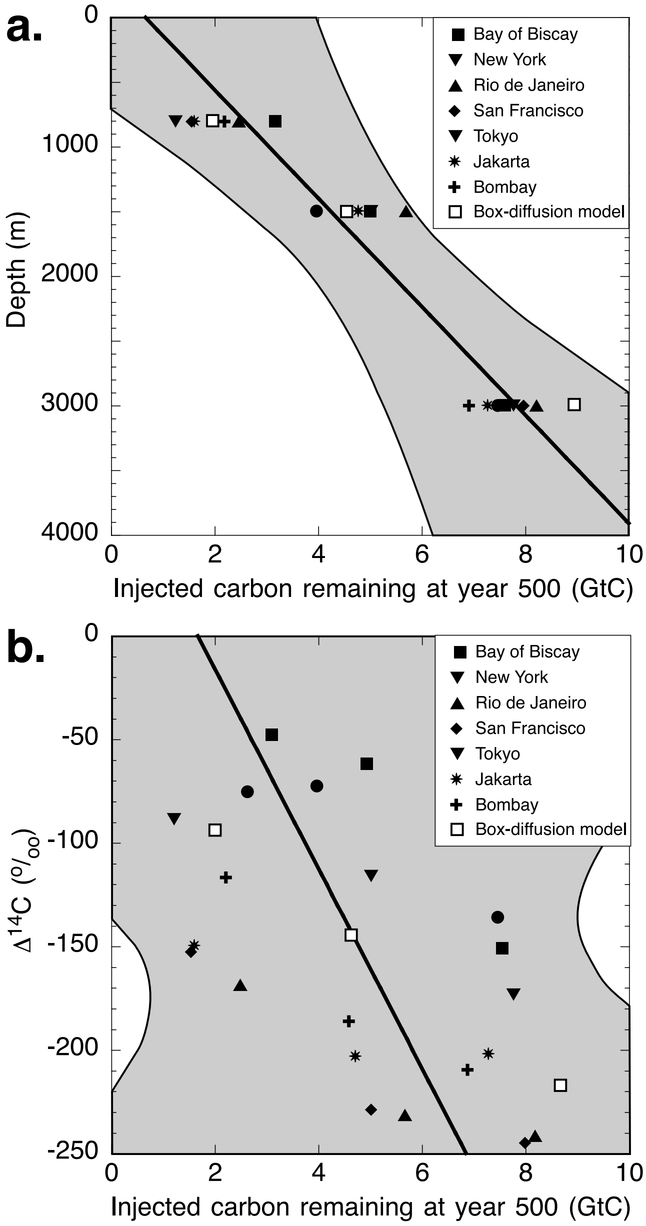

Figure 2. Injected carbon remaining in the ocean at year 500 versus (a) depth and (b) natural $\Delta^{14}C$ at the location of carbon injection. Filled symbols refer to simulated injections at different locations in the three-dimensional ocean model. The open squares show box-diffusion model results. The shaded gray areas represent the 95% prediction interval for an individual value of injected carbon remaining at year 500 based on (a) depth and (b) natural $\Delta^{14}C$ in the 3-D model simulations. Depth alone provides a relatively good prediction of injected carbon remaining in the 3-D ocean model at year 500, whereas radiocarbon alone provides little predictive capability.

injection in other ways. For example, radiocarbon has proven to be a useful tool in helping to develop our understanding of ocean circulation and in helping to diagnose and evaluate the ocean circulation simulated in models [*Toggweiler et al.*, 1989; *Guildersen et al.*, 2000].

5. Conclusions

[18] In our simulations, we find that:

1. The radiocarbon content alone at a given location in the ocean is a poor predictor of how effective injection of CO_2 at that location is at sequestering carbon away from the atmosphere.

2. The depth of injection alone, in contrast, is a relatively good predictor of the effectiveness of the CO_2 injection.

3. Mean retention of injected carbon in the upper ocean is well predicted by a one-dimensional box-diffusion model, but injections >3 km may require representation of advection.

[19] These results suggest that the expected time for a water parcel to return to the surface increases with depth, but is not in general related to the amount of time since that parcel was last at the surface.

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K. Caldeira, M. E. Wickett, and P. B. Duffy, Climate and Carbon Cycle Modeling Group, Lawrence Livermore National Laboratory, 7000 East Ave., L-103, Livermore, CA 94550, USA. (kenc@llnl.gov; wickett@llnl.gov; pduffy@llnl.gov)